

REMARKS

Rejection of Claims and Traversal Thereof

In the October 5, 2004 Office Action, claims 1-17 were rejected under 35 U.S.C. §103(a) as being unpatentable over XP-002161407 (Rogowin S. A.). Applicants traverse such rejection and submit that Rogowin does not meet the standard required to render the presently claimed invention obvious.

Rejections under 35 U.S.C. §103(a)

According to the Office:

"Rogowin S.A. teaches that it is known that bleached cellulose exhibits discoloration and decomposition at high temperatures due to the presence of carboxyl groups. This problem is present regardless what type of bleached cellulose is used or whether a particular solvent is possibly decomposed with the cellulose. This decomposition would occur whether the cellulose is heated in the dry state or in a solution."

Applicants vigorously disagree with the blanket statement made by the Office. Initially, it should be noted that the Rogowin reference was published in 1960 and before lyocell was even invented. Thus, this reference discusses production of artificial fibers, but there is no mention of the lyocell process as in the presently claimed invention.

Applicants' claim 1 is as follows:

1. A process for manufacture of cellulose mouldings with reduced cellulose decomposition from TCF-bleached or ECF-bleached cellulose, comprising:

dissolving a bleached cellulose pulp having a **reduced number of carboxyl groups in an aqueous tertiary aminoxide to form a bleached cellulose solution, wherein the reduced number of carboxyl groups causes reduced decomposition of the bleached cellulose in the process,** and wherein the bleached cellulose is selected from the group consisting of:

Total Chloride-Free (TCF)-bleached cellulose comprising a carboxyl group content in the range from 1 to 35 $\mu\text{mol/g}$ and Elementary Chloride-Free (ECF)-bleached cellulose comprising a carboxyl group content in the range from 1 to 50 $\mu\text{mol/g}$; deforming the cellulose solution; and

coagulating the deformed solution to generate a spinning solution for forming the cellulose moulding.

Thus, applicants' claimed invention comprises using a bleached cellulose pulp dissolved in an aqueous tertiary aminoxide solvent wherein the bleached cellulose has a reduced number of carboxyl groups and because of this reduced number of carboxyl groups there is reduced decomposition of the bleached cellulose. The presently claimed invention is very different from that described in the cited Rogowin reference.

A discussion is set forth in the Rogowin reference regarding blocking the carboxyl groups with calcium ions in water (See translation of article in Appendix A). The reference discusses that to increase light resistance and thermostability of the fibres, the carboxyl groups are blocked. Applicants question, after reading the Rogowin reference, why a skilled artisan would even consider reducing the amount of carboxyl groups, especially in light of the results set forth in Table 33. Specifically, the results in Table 33 showed beneficial results for the two cellulose pulps labeled "II." These pulps have the larger number of carboxyl groups and by merely blocking the carboxyl groups with a calcium ion, there was only a 4.9 and 4.8 percent reduction in polymerization. In contrast, the two cellulose pulps labeled "I" had a smaller amount of carboxyl groups and these carboxyl groups were unblocked, but when the pulp was heated the polymerization of the cellulose was reduced about 25%. It is evident from the teachings of this reference that a smaller number of carboxyl groups (unblocked) in fact was detrimental to the polymerization process and polymerization was negatively impacted by a reduction in polymerization. Clearly, these statements and results made by Rogowin cannot be ignored by the Office.

Considering the problems or reduced polymerization due to reduced carboxyl groups, applicants suggest that the cited reference teaches away from applicants' claimed invention. The Court in *In re Gurley*, 31 USPQ2d 1131 (Fed. Cir. 1994) addressed this very issue and stated:

“[I]n general, a reference will teach away if it suggest that the line of development flowing from the reference's disclosure is unlikely to be productive of the result sought by the applicant. See *United States v. Adams*, 383 U.S. 39, 52, 148 USPQ 479, 484 (1966) (“known disadvantages in old devices which would naturally discourage the search for new inventions may be taken into account for determining obviousness.”)

Surely, anyone skilled in the art reading the Rogowin reference would be discouraged from going in the direction that applicants have gone.

Further, from the results set forth in Table 33, why would one even consider reducing the carboxyl groups, when instead, by using a blocking calcium group the polymerization was maintained. Clearly, polymerization is important and one skilled in the art, seeing the results of Table 33 would consider blocking the calcium rather than reducing the numbers of carboxyl groups because it is very evident that by not blocking the carboxyl groups, the problem of reduced polymerization is exacerbated. Notably, the last statement made in this section (7.314) of the reference states: “[c]onsequently, to obtain an increase of the light resistance and thermostability of the obtained fibres, the carboxyl groups have to be blocked in the starting pulp or the hydrate pulp.” Further, the reference discusses that even though there are more carboxyl groups on unbleached viscose fibres, it took longer for these fibres to yellow due to the calcium blocking relative to a bleached sample with less carboxyl groups. Thus, it is very clear that this reference provides no incentive to reduce the carboxyl groups.

The Office assumes that a reference that discusses behavior of viscose fibers is applicable to that of lyocell fibers. As stated above, lyocell fibers were not even imagined at the time of the Rogowin reference. Further, it is very well known in the art that viscose and lyocell do not exhibit the same properties and in fact are very different cellulose products. As such, the Office cannot make a blanket statement that would automatically group the two products together in all instances. Clearly, at the time of the Rogowin reference, written many years before the discovery of lyocell, there was no indication that characteristics and/or properties of viscose could be transferred to all known or yet undiscovered cellulose products. Woodings in 1995 (copy in Appendix A) discussed the differences between the newly discovered lyocell relative to viscose. Specifically, at page 306, column 2, Woodings discussed that lyocell and viscose were so different that lyocell deserved a separate marketing strategies. Further, it is stated that lyocell as a “1.5 denier fibre, it could be spun into yarns with a better strength conversion factor than other cellulosic fibres, allowing rotor-spun lyocell to out-perform ring-spun cotton or modal viscose.” A more recent article by Colom (2002) clearly sets forth the differences between viscose and lyocell. As stated at page 2229, column 2, “[i]t has been observed that during the mercerisation treatment the viscose type fibres are more affected to the degradation caused by the transformation of crystalline cellulose II to amorphous cellulose, to the point of total dissolution at high caustic concentrations for modal and viscose. For lyocell fibres, this transformation is partial and dissolution at high concentrations does not occur. This can be

explained by the orientation and high crystallinity of the lyocell macromolecules.” Applicants could provide multiple additional references that discuss the differences between these cellulosic products, however, redundancy is not necessary to show that one skilled in the art would certainly recognize that cellulose products are different and that a reference discussing a viscose product is not applicable to a lyocell process or product.

Applicants question that since the cited reference relates to viscose, how could a skilled artisan make any modification to such a reference to arrive at an invention that possesses such heretofore unknown characteristic? That which is unknown cannot be obvious. Clearly, a skilled artisan looking for an improvement of the discoloration of cellulose with the lyocell process has no reason to start from a document with no relevance to the lyocell process.

Further, the Office has cited a reference that discusses behavior of dry cellulose and attempts to compare this reference to the presently claimed invention that is a cellulose suspension in an aqueous tertiary aminoxide solvent. Rogowin relates to the reaction of pure cellulose during dry heating. On the other hand, the presently claimed invention relates to the behavior of aqueous solution of cellulose dissolved in an aqueous tertiary aminoxide, such as NMMO. Clearly, the behavior of a dry substance cannot be compared to the dissolved cellulose of the presently claimed invention.

It should be noted that U. S. Patent No. 4,426,228 (corresponding EP 0 047 929 was cited by the International Examiner) discloses that there are great differences between cellulose that is dissolved (which means that the intermolecular hydrogen bridge bonds have been destroyed) and undissolved cellulose (which means that the structure of the hydrogen bonds between the polymer molecules is preserved) (see column 2, lines 54-61). Obviously, dried cellulose shows the structure of undissolved cellulose. Thus, the behavior of cellulose depends on the chemical environment and the Office cannot speculate to the behavior of a composition by the limited disclosure of the cited reference.

In light of the above discussion and the fact that (1) there is no motivation to modify the cited reference to go in the direction of applicants' claimed invention, (2) each and every recited limitation of applicants' claimed invention is not disclosed or suggested in the cited reference; and (3) the cited reference teaches away from going in the direction of applicants' claimed

invention, it is clear that the cited reference fails to establish a *prima facie* case of obviousness of applicants' claimed invention.

Conclusion

Applicants have satisfied the requirements for patentability. All pending claims are free of the art and fully comply with the requirements of 35 U.S.C. §112. It therefore is requested that Examiner Osele reconsider the patentability of all pending claims in light of the current amendment, and withdraw all rejections, thereby placing the application in condition for allowance. Notice of the same is earnestly solicited. In the event that any issues remain, Examiner Osele is requested to contact the undersigned attorney at (919) 419-9350 to resolve same.

Respectfully submitted,

A handwritten signature in cursive script, appearing to read "Marianne Fuierer", is written over a horizontal line.

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XP-002161407

168 Methods for production of artificial fibres

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7.314 Aldehyde and carboxyl groups.

As a result of oxidative side reactions, which happen during the cellulosic bleaching, aldehyde and carboxyl groups may occur aside of hydroxyl groups in cellulosic macromolecules. Occurrence of carboxyl groups may be also explained by forming of mixed macromolecules, containing uronic acids, formed during the biochemical synthesis.

The aldehyde groups formed in the cellulosic molecules are quantified by the copper or iod number and showing an important influence with respect to the alkaline resistance and thermo resistance of the cellulose. The more the amount of aldehyde groups, the less the resistance of cellulose against alkalines and the cellulose will be more intensively decomposed by the treatment with alkalines, especially during the mercerisation. Further, aldehyde groups effect the discoloration of cellulose at higher temperatures [14]. The higher the number of aldehyde groups, the more yellow the cellulose at higher temperatures (40 to 60 min at 110°C).

The carboxyl groups decrease the thermostability of cellulose and the fibres made thereof. Table 33 shows data [15] about the changes of the polymerisation degree of cellulose having a small content of carboxyl groups (0,004 to 0,1 %) after heating to 105°C over one hour.

Table 33 Influence of the content of carboxyl groups in cellulose of the polymerisation degree of cellulose after heating

Cellulose	Content of COOH-groups of the cellulose [%]	Decrease of the polymerisation degree after heating, based on the primary polymerisation degree [%]
Beech tree pulp I	0,004	24,8
Beech tree pulp II	0,046	4,9
Pine tree pulp I	0,004	28,3
Pine tree pulp II	0,1	4,8

In the samples marked by II the free carboxyl groups are calcium blocked by washing with water.

As shown by the data of the Table small amounts of COOH-groups cause the degregation of cellulose by heating. By blocking said groups the intensity of said thermal degregation is substantially decreased. Further, the influence of the carboxyl groups is shown in that the light resistance of the cellulose and the fibres made thereof is decreased. Thus, e.g. unbleached viscose fibres having I COOH-groups on 500 to 550 elementary elements, and a sample bleached with H_2O_2 (1,5 g/l) having I COOH-groups on 300 to 370 elements, are colored to yellow during a longer drying period.

Consequently, to obtain an increase of the light resistance and thermostability of the obtained fibres, the carboxyl groups have to be blocked in the starting pulp or the hydrate-pulp.

7.315 Lignin

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The development of advanced cellulosic fibres

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For the majority of the last century, commercial routes to regenerated cellulose fibres have coped with the difficulties of making a good cellulose solution by using an easy to dissolve derivative (e.g. xanthate in the case of viscose rayon) or complex (e.g. cuprammonium rayon). For the purposes of this paper, advanced cellulosic fibres are defined as those made from a process involving direct dissolution of cellulose. The first examples of such fibres have now been generically designated as lyocell fibres to distinguish them from rayons, and the first commercial lyocell fibre is Courtaulds' Tencel.

Keywords: cellulose; fibre; lyocell

Reviews of the early work on direct dissolution have been produced by Turbak^{1,2}. He records the efforts to dissolve cellulose directly as a *base* using phosphoric, sulfuric and nitric 'protonic' acids, or using zinc chloride, thiocyanates, iodides and bromides as Lewis acids. With regard to cellulose acting as an *acid*, he lists sodium zincate, hydrazine, and sodium hydroxide as inorganic solvents, and quaternary ammonium hydroxides, amines, dimethylamine/dimethylsulfoxide mixtures and amine oxides as organic bases. He obtained 16% cellulose solutions in lithium chloride/dimethylacetamide systems³ and 14% solutions in dinitrogen tetroxide/dimethylformamide systems⁴. Cuculo and Hudson⁵ obtained solutions of up to 14% cellulose in an extensive study of the ammonia/ammonium thiocyanate solvent system. The dimethylsulfoxide/paraformaldehyde system, discovered by Johnson and Nicholson⁶, proved capable of dissolving cellulose with a wide range of degrees of polymerization without causing degradation. However, despite early promise, the problems of developing fibre production routes using these systems have so far proved insurmountable, with the single exception of the amine oxide route.

The cellulose-dissolving potential of the amine oxide family was first realized⁷ in 1939, but it was not until 1969 that Johnson described the use of cyclic mono(*N*-methylamine-*N*-oxide) compounds (e.g. NMMO: Figure 1) as a solvent-size for strengthening paper⁸ by partially dissolving the cellulose fibres.

Other Johnson patents^{9,10} covered the preparation of cellulose solutions using NMMO and speculated about their use as dialysis membranes, food casings (sausage skins), fibres, films, paper coatings and non-woven

binders. NMMO emerged as the best of the amine oxides and its commercial potential was demonstrated by Franks and Varga^{11,12} of American Enka. Chanzy *et al.* at the Plant Macromolecules Research Centre (CERMAV-CNRS) in Grenoble have studied the cellulose/NMMO system in depth¹³; a recent paper indicates that further strength increases can be obtained by adding ammonium chloride or calcium chloride to the dope¹⁴.

Both American Enka¹⁵ and Courtaulds set up pilot plant work in the early 1980s with the objectives of developing the fibre spinning and solvent recovery operations. To date, only Courtaulds has proceeded to full commercial scale (see next section). The Austrian viscose producer Lenzing studied various systems¹⁶ and commenced pilot operations on an NMMO system at the end of the 1980s, but has yet to announce a commercial plant.

Work on other routes to cellulosic fibres continues, driven by a desire to identify an environmentally benign route to cellulosic fibres which will utilize the large capital investment in the xanthate route and hence cost less than a completely new fibre process.

Chen, working on a small scale at Purdue University, claims that solutions containing 10–15% cellulose in 55–80% aqueous zinc chloride can be spun into alcohol

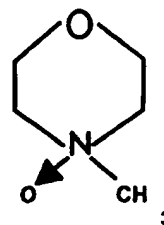


Figure 1 *N*-methyl morpholine-*N*-oxide (NMMO)

'Tencel' and 'Galaxy' are trademarks and/or registered trademarks of the Courtaulds group of companies

or acetone baths to give fibres with strengths of 1.5 to 2 g/den (g, grams, den, denier). However, if these fibres were strain-dried (i.e. stretched) and rewetted whilst under strain, strengths of 5.2 g/den were achieved¹⁷.

Kamide *et al.* at Asahi have been applying the steam explosion treatment¹⁸ to dissolving pulp to make it dissolve directly in sodium hydroxide¹⁹. In recent papers^{20,21}, they claimed to have obtained a 5% solution of steam-exploded cellulose in 9.1% NaOH at 4°C being spun into 20% H₂SO₄ at 5°C. The apparently poor fibre properties (best results being 1.8 g/den tenacity dry, with 7.3% extension) probably arise because the fibres were syringe extruded at 75 denier/filament. Asahi feel that this could be the ultimate process for large-scale production of regenerated cellulose fibres.

The Courtaulds' lyocell process

The increasing costs of reducing the environmental impact of the viscose process coupled with the increasing likelihood that the newer cellulose solvents would be capable of yielding a commercially viable fibre process led Courtaulds Research to embark on a systematic search for a new fibre process in the late 1970s. The project, codenamed 'Genesis', did not involve basic research into new solvents for cellulose so much as screening the known solvents against criteria felt to be important for the cellulosic fibre process of the future. The solvent chosen had to be recyclable at a very high level of efficiency, and hence as near to totally containable in the process as possible. It had to be safe to work with and safe in the environment in the event of any losses. It had to be able to dissolve cellulose completely without reacting with it or degrading it, and the resulting process had to be less energy-intensive than the viscose route, which had already been proven to be less energy-intensive than synthetic fibres in an independent study. It was especially important to choose a system which, like the melt-spun synthetic fibres system, would not require costly gaseous or liquid effluent treatment systems. Finally, the process had to be capable of making good textile fibres to maintain, or even extend, the cellulosic fibre share of the global market, against fierce competition from melt-spun synthetic fibres based on cheap but non-renewable oil reserves.

By 1980, NMMO had been shown to be the best solvent, provided well-known difficulties associated with its thermal stability could be avoided by appropriate chemical engineering. Filaments obtained from the first single-hole extrusion experiments had promising properties, so Courtaulds committed the resources (1982) to build the first small pilot plant to test the feasibility of overcoming the solvent-handling and recovery problems which had prevented earlier commercial exploitation. This system, capable of making up to 100 kg/week of fibre, met its objectives and allowed the first serious end-use development to begin. Scale-up to a 1000 kg/week pilot line was possible in 1984, and a 25000 kg/week semi-commercial line was commissioned in 1988 to allow a thorough test of the engineering and end-use development aspects.

Comparisons of lyocell with viscose in both laboratory and test markets proved that the fibres were sufficiently

different to deserve separate marketing strategies. Lyocell was:

- stronger than any other cellulosic fibres, especially when wet
- easy to process into yarns and fabrics alone or in blends
- easy to blend (unique fibre presentation)
- easy to spin to fine count yarns
- very stable in washing and drying
- thermally stable
- easy to dye to deep vibrant colours
- capable of taking the latest finishing techniques to give unique drape
- comfortable to wear

As a 1.5 denier fibre, it could be spun into yarns with a better strength conversion factor than other cellulosic fibres, allowing rotor-spun lyocell to out-perform ring-spun cotton or modal viscose. Fabrics could be made at high efficiency, and proved to have the anticipated tear and tensile advantages over other cellulosic fibres. Direct, reactive or vat dyes could be used, and easy-care properties could be achieved with less resin finish than normal. Lyocell could therefore be marketed as a new premium-quality clothing cellulosic fibre and not simply as a long-term replacement for viscose.

The Courtaulds semi-commercial production system is illustrated in Figure 2. Dissolving grade woodpulp is mixed into a paste with NMMO and passes through a high-temperature dissolving unit to yield a clear viscous solution. This is filtered and spun into dilute NMMO, whereupon the cellulose fibres precipitate. These are washed and dried, and finally baled as staple or tow products as required by the market. The spin-bath and wash liquors are passed to solvent recovery systems which concentrate the NMMO to the level required for re-use in dissolution.

As mentioned above, the new fibre has physical properties (Table 1) which are sufficiently different from regular rayon to allow an initial market development strategy which does not erode the position of the traditional viscose fibre. The unique strength, texture and

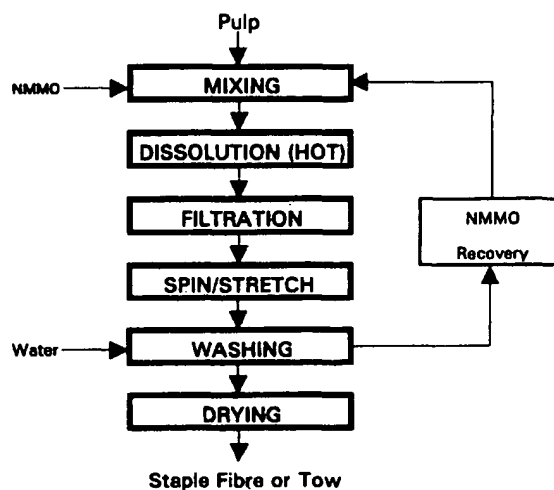









Figure 2 Direct dissolution: Courtaulds' lyocell

Table 1 The properties of selected commercial rayon fibres

Property	Cuprammonium	Regular rayon	Improved rayon	Modal	Polynosic	'Y'-shaped rayon ^a	Solvent-spun rayon ^b
Fibre cross-section							
Dry tenacity (cN/tex)	15-20	20-24	24-30	34-36	40-45	18-22	40-44
Extensibility at break % (dry)	7-23	20-25	20-25	13-15	8-12	17-22	14-16
Wet tenacity (cN/tex)	9-12	10-15	12-16	19-21	30-40	9-12	34-38
Extensibility at break % (wet)	16-43	25-30	25-35	13-15	10-15	23-30	16-18
Water imbibition (%)	100	90-100	90-100	75-80	55-70	100-110	65-70
Cellulose D.P.	450-550	250-350	250-350	300-500	550-700	250-350	550-600
Initial wet modulus (@ 5%)	30-50	40-50	40-50	100-120	140-180	35-45	250-270

^aThe 'Y'-shaped rayon data are based on Courtaulds' Galaxy fibre

^bThe solvent-spun rayon data are based on Courtaulds' Tencel fibre

coloration potential of the fibre enable it to command premium prices for upmarket men's and ladies' outerwear. The existing process will also be capable of meeting the needs of the industrial, non-woven and specialty paper markets as these end-uses are developed. Several studies of its performance in non-woven fabrics show it capable of yielding fabric strengths between two and three times higher than hitherto possible with regenerated cellulosic fibres^{22,23}. It appears particularly suitable for the latest hydroentanglement systems²⁴ where its basic strength and ability to develop a micro-fibre surface under the action of high-pressure water jets enable it to be made into very strong non-woven fabrics with textile-like properties.

Continuous operation of the 25 000 kg/week semi-commercial line provided the necessary confidence in both process and market to justify full commercial operation. An 18 000 tonne/year line was therefore designed and built in Mobile (Alabama, USA) in 1991/1992. Since its commissioning in May 1992, this plant has approached its target productivity and quality, and is now supplying fibre to several major clothing markets. It is set up to be capable of making the range of fibre deniers and lengths required for premium-quality textiles and non-woven fabrics. In the summer of 1995, the capacity of the Mobile plant was more than doubled. Plans for a second plant in Europe are already advanced, and the options for a third plant in the Far East are being investigated.

Environmental issues

Fibre production

Cellulose is the natural polymer which makes up the living cells of all vegetation. It is the material at the centre of the carbon cycle, the most abundant and renewable biopolymer on the planet. Rayon fibre producers have converted it into fine textile fibres used for almost a century but rayon remains unique among the mass-

produced manmade fibres because it is the only one to use the natural polymer directly. Cellulosic fibres therefore have much to recommend them provided that the processes used to make them have minimal environmental impact.

The solvent-spun process, as currently designed, will use the same sources of pulp (at slightly higher levels of efficiency) as the viscose process. Alternative pulping sequences which eliminate all chlorine compounds from the process are being investigated for use in both viscose and solvent systems.

Amine oxide solvent. *N*-methylmorpholine *N*-oxide (NMMO) is the solvent used. It is manufactured by methylation and oxidation of morpholine, which comes from a reaction between diethylene glycol and ammonia. This is the only major chemical used in the solvent-spun process, and its consumption is reduced to the absolute minimum by recycling, which is made possible by solvent recovery.

Energy. Early attempts to assess the total energy required to make baled staple fibre from naturally occurring raw materials (wood in the case of cellulosic fibres and oil in the case of synthetic fibres) used differing approaches and were insufficiently rigorous to allow hard conclusions to be drawn. In general, the authors²⁵⁻³⁰ subdivided the fibre production sequence into monomer making, polymer making and fibre production, and, while a variety of fibres are covered, only viscose rayon and polyester are mentioned in all of these publications. Tonnes of fuel-oil-equivalent per tonne of fibre (TFOE/T) were the most popular units, with rayon requiring from 1.7 to 2.4 TFOE/T and polyester requiring 2.6 to 4.2 TFOE/T.

The studies all concluded that rayon required less energy to make than polyester, but there was little agreement on the magnitude of the difference. The wet-spun cellulosic fibres required more energy than

melt-spun polyester for the fibre-making step, but they had no monomer energy requirement. The 'polymerization' requirement was therefore minimal. In the case of the 1.7 TFOE/T figure for rayon, full credit was being given for the fact that the pulp mill energy needs were renewable and not dependent on fossil fuels. Pulp could be fed directly into the viscose process without incurring any transport or drying cost, and the pulp mill could be driven entirely by energy obtained from burning the parts of the tree which were not needed in the final product. This 'free' and renewable energy was not counted.

From an energy viewpoint, the solvent route to cellulosic fibres is identical to the viscose route up to the point where the cellulose enters the solvent. The energy requirement for the non-cellulosic raw materials is significantly lower in the case of the solvent route, but the solvent route requires similar energy levels for dope handling, spinning, washing and recycling. The lower water imbibition of the solvent fibre (65% versus 95%) yields savings in fibre drying and of course in any subsequent washing and drying operations.

Overall, the solvent route shows a useful economy in this important resource when compared with viscose production on the same scale.

Fossil reserves. Renewable resources will become increasingly important as the planet's stocks of fossilized reserves are depleted and as governments realize that biomass can provide a truly sustainable, cost-effective source of energy and materials. As indicated above, the recycling rate is so high that solvent usage is kept down to a few kg per tonne of fibre, and hence fossil reserve dependence is minimal.

Gaseous effluents. The solvent process involves direct dissolution of cellulose in a liquid which is recycled very efficiently. There are no chemical reactions and no by-products of the sort which are unavoidable in the regeneration of cellulose from the viscose route.

The solvent process produces very little atmospheric emission. Traces of volatile organic compounds associated with the solvent and the soft finish leave the plant in the normal course of ventilation.

Liquid effluents. The solvent route uses much less water than the viscose process and the process effluent needs significantly less treatment.

Fibre disposal

Cellulosic fibres, like the vegetation from which they arise, can become food for micro-organisms and higher life forms: in other words, they biodegrade. In complete biodegradation or incineration, the final breakdown products are carbon dioxide and water; these disposal methods simply recycle the cellulose to the atmospheric components from which it was made.

It is also possible to liberate and use some of the 'free' solar energy which powered the manufacture of sugars and cellulose during photosynthesis. This can be achieved by burning or by anaerobic digestion. Slow anaerobic biodegradation occurs in all landfill sites dealing with municipal solid waste. This process generates methane from cellulose, which can be burnt to drive gas turbines. If future landfills are lined and operated with moisture

addition and leachate recycling, then energy generation and the return of landfill sites to normal use can be accelerated³¹.

Commercial issues

In the last ten years, viscose-based staple fibres have, like the cuprammonium and viscose filament yarns a decade earlier, ceased to be commodities. They have been repositioned in the market from low-cost textile fibres which were used in a myriad of applications regardless of suitability, to premium-priced fashion fibres delivering comfort, texture and attractive colours in ways which are hard to achieve with synthetic fibres. They are still widely used in blends with polyester and cotton to add value, whereas a decade ago they would have been added to reduce costs.

Such repositioning inevitably means reduced production volume, and, for the first time this century, production in the last decade has been below that a decade earlier (Figure 3). Most capacity reductions have been in North America and in Europe, especially the Eastern part. This has been offset in part by capacity increases in the Far East. Rayon is no longer a major component of carpets, and has lost the disposable diaper (nappy) coverstock business to cheaper and more easily processed polypropylene. However, it has gained a share in health and hygiene products and is now a major component of tampons worldwide.

The lyocell fibres now being introduced have the capability to halt the overall decline in manmade cellulosic fibres' share of the world market. In clothing textiles, Courtaulds' Tencel™ had early successes in market sectors which were previously closed to the other manmade cellulosic fibres. The combination of the unique fibre properties with novel fabric and garment finishing techniques yielded highly desirable garment aesthetics. These aesthetics have proved attractive in garments as diverse as denim and underwear.

In non-woven fabrics, lyocell's inherent strength and 'bondability' have led to a variety of new applications which were not possible with viscose rayon. In hydro-entanglement, one of the fastest growing sectors of the non-woven industry, the use of Courtaulds' lyocell is now showing several advantages over other cellulosic fibres. Compared with viscose or cotton, it allows the

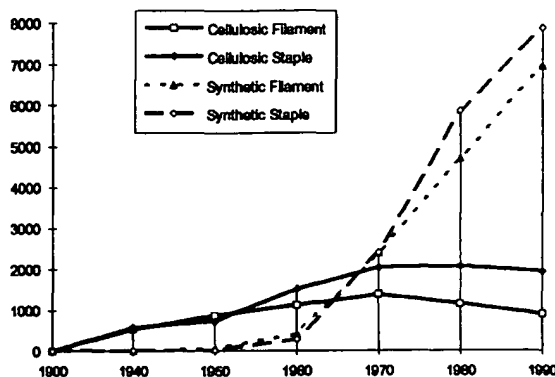


Figure 3 World manmade fibre production: 1900-1990

manufacture of a wider range of basis weights, with higher strengths, better appearance and improved dry and wet textures. At high bonding pressures, it has enabled the production of non-woven fabrics which are stronger than the same weight of woven cotton. When fibrillated by refining or very-high-pressure hydroentanglement, the microfibrils generated may be used in leather- or suede-like materials, efficient filters, or even durable papers.

Conclusion

Rayon fibres, made for a century by the direct conversion of abundant vegetable matter, have always had much to recommend them in textiles compared with synthetic fibres made from fossil fuels. The renewability of their main raw material, their overall energy efficiency, their lack of dependence on fossil fuels, their long history of safe use in hygiene applications, and their easy disposal and natural recyclability make them strong contenders for tomorrow's textile industry also.

The new solvent route to rayon reinforces these inherent strengths by using a modern fibre production system, which, being physical rather than chemical, reduces environmental impact to a minimum. The Tencel investment, coupled with continuous improvement of the traditional route, gives us what we believe is a winning approach to textile industry fibre supply for some time to come.

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Crystallinity changes in lyocell and viscose-type fibres by caustic treatment

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Abstract

One of the most important treatments performed on cellulosic fibres to improve properties such as dimensional stability, tensile strength and lustre, is mercerisation. The aim of this work was to study the crystallinity, accessibility and unit cell structure changes occurring in three types of regenerated cellulose fibres (lyocell, modal and viscose) that were mercerised with caustic soda solutions of different concentrations. Differences were observed between the behaviour of the viscose type fibres (viscose and modal) and that of the lyocell fibres. For the viscose type fibres, the proportion of crystalline regions increased at low alkali concentrations, while for lyocell fibres a decrease in crystallinity was observed. In all three fibres there was a transformation from cellulose II to amorphous cellulose. While for lyocell the transformation was partial, the modal and in particular the viscose fibres showed a complete transformation, and the swelling agent caused the fibre to dissolve at high caustic concentrations.

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1. Introduction

Over the years, much effort has been spent on finding an artificial silk and several different cellulose derivatives have been examined. However, only two (acetate and xanthate ester) are of commercial importance today. Both have been used for many decades in the regeneration of wood cellulose to form fibres and films. Recently, however, there has been intensive research into the commercial regeneration of cellulose due to the environmental problems associated with the xanthate process [1]. Among the many aqueous and non-aqueous cellulose solvent systems reported in the past three decades, only *N*-methyl-morpholine-*N*-oxide (NMMO) has been successfully used in the production of regenerated cellulose textile fibres [2]. The fibres regenerated from NMMO solutions, known with the generic name of lyocell [3],

have higher crystallinity and amorphous orientation. This yields cellulose fibres with higher wet strength than those produced using the earlier technologies [4].

The swelling of regenerated cellulose in alkali solutions has been applied industrially for many years. This process causes changes in the crystallinity, accessibility, unit cell structure, and orientation of fibrils in cellulosic fibres. The extent to which sodium hydroxide solutions change these properties depends on factors such as the concentration of the sodium hydroxide solution, the temperature, the degree of polymerisation, the source of the cellulose, the physical state of the cellulose (i.e., fibre, yarn or fabric), and the degree of tension employed to restrict or promote fibre shrinkage and swelling. These variables have been effectively controlled for the mercerisation of cotton along with other celluloses and blends of synthetic fibres and cellulose in order to improve or optimise one or more of the following properties: dimensional stability, affinity for dyes, tensile strength, higher add-on of finishing agents, lustre and fabric smoothness [5].

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In cellulose samples that have been subjected to a mercerisation process, the relative amounts of crystalline and amorphous regions and the amounts of cellulose I and cellulose II vary simultaneously. In order to follow this process, the infrared ratios proposed by O'Connor et al. [6,7] were used. They suggested that the regions $1372\text{--}1375\text{ cm}^{-1}$ (CH-bending) and 2900 cm^{-1} (CH-stretching) to be the most suitable for indicating crystallinity changes. This is a good method for studying changes in the microstructure, for example, when treating cellulose with sodium hydroxide, where there should be a decrease in the crystalline index or conversion of the cellulose I structure to cellulose II and amorphous structure.

The aim of this study was to compare the changes in the supermolecular structure and the accessibility of the three different regenerated cellulose fibres (viscose and modal, obtained from the xanthate process, and lyocell, based on the solvent NMMO process) which were treated with sodium hydroxide. The purpose of this study was to better understand fibre microstructure behaviour and to find ways to further improve its properties.

2. Experimental

2.1. Materials

Lyocell, viscose and modal staple fibres of 1.7 dtex, supplied by Lenzing Lyocell were used.

2.2. Caustic soda treatment

The samples were washed in a sodium carbonate solution (2 g/l) for 30 min at $30\text{ }^{\circ}\text{C}$. They were then wrung out, rinsed with distilled water and dried at $105\text{ }^{\circ}\text{C}$ for 2 h. Two and a half grams of the dried fibres were treated for 30 min with different NaOH solutions at $20\text{ }^{\circ}\text{C}$, with a bath ratio of 11:1. Caustic concentrations in the bath were 6.2, 12.4, 16.7, 17.7, 18.0, 21.4, 24.0, 30.0, 40.0 and 50.0 g NaOH/100 ml respectively. When the treatment period was over, the various fibres were wrung out, rinsed and air-dried at $40\text{ }^{\circ}\text{C}$.

2.3. Moisture regain

The moisture regain measurements, taken from the dry side, were obtained after the desiccation (over P_2O_5) of the samples at room temperature over three days, followed by conditioning for one week over a saturated magnesium acetate solution at $20\text{ }^{\circ}\text{C}$ (RH: 65%) [8].

2.4. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra were obtained by means of a spectrometer Nicolet Avatar 320 with CsI optics. Samples of the finely divided material (1.5 mg) were ground and dispersed in a matrix of KBr (100 mg). A pellet was then formed by compression at 167 MPa. The sample collection was obtained using 100 scans and a resolution of 2 cm^{-1} .

3. Results and discussion

3.1. Spectral study of regenerated cellulose fibres

Previous work demonstrates, by means of various methods (X-rays, IR), that the cellulose fibres are made up of a mixture of three components, these being crystalline cellulose I, crystalline cellulose II and amorphous cellulose [9]. The differences observed in the mechanical and chemical behaviour of different fibres lead us to believe that these fibres, which have similar chemical compositions, differ in the percentage composition of each component, thus allowing specific conformations with some structural differences.

The infrared spectra in the $1660\text{--}870\text{ cm}^{-1}$ region of the three regenerated cellulose fibres studied are shown in Fig. 1. This region contains the largest number of spectral differences, which allows for the identification of the structural changes in the cellulosic fibres. Table 1 shows the most significant bands that were studied and analysed, and their corresponding assignments.

The absorption bands indicated in Fig. 1 are assigned mainly to crystalline cellulose II and amorphous cellulose. The 1420 cm^{-1} band is characteristic of both cellulose II and the amorphous cellulose. If a cellulose fibre

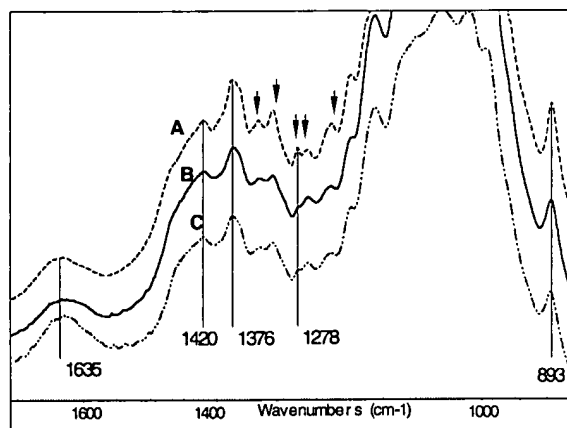


Fig. 1. Spectral area of $1660\text{--}870\text{ cm}^{-1}$ corresponding to the fibres such as: (A) lyocell, (B) modal and (C) viscose.

Table 1
Characteristic absorption bands of regenerated cellulose fibres

Wavenumber (cm ⁻¹)	Assignment
1420	δ CH ₂ symmetric bending
1376	C–H bending
1336	C–OH in plane bending
1316	CH ₂ wagging
1278	C–H bending
1235	C–OH in plane bending
1227	C–OH in plane bending
893	γ (COC) in plane, symmetric stretching

has a significant amount of crystalline cellulose I, this band moves toward 1430 cm⁻¹ and the amounts of cellulose II and amorphous cellulose decreases. The absence of an appreciable band at 1430 and at 1111 cm⁻¹ indicates that crystalline cellulose I is practically non-existent in the regenerated cellulose fibres.

Bands 1336 and 1316 cm⁻¹ (marked by arrows in Fig. 1) show significant differences in their absorbances. The 1316 cm⁻¹ band assigned to both crystalline celluloses (Cel I and Cel II) is much more intense in the lyocell fibre than in the other two fibres.

The absorption bands at 1336, 1316, 1278, 1262, 1234 and 1227 cm⁻¹ in regenerated cellulose fibres are due to differences in their structural composition and relative amount of each constituent. Nelson et al. [6] found that the bands 1336, 1316, 1278 and 1227 cm⁻¹ showed the greatest differences between the crystalline cellulose II and the amorphous cellulose, and Kondo et al. [10] demonstrate that these bands were not characteristic of the amorphous area. As can be seen, the absorption bands at 1336, 1316, 1278 and 1227 cm⁻¹ show peaks of greater intensity for the lyocell fibres. This shows that the ratio of crystalline cellulose II to amorphous cellulose in lyocell fibres is greater than that of modal and viscose.

Table 2 shows the infrared crystallinity index results obtained for lyocell, viscose and modal fibres. These indexes have been calculated by the infrared ratios

proposed by Nelson and O'Connor [6,7], a_{1376}/a_{2902} (total crystalline index (TCI)) and a_{1420}/a_{893} (lateral order index (LOI)), and the doublet a_{1278}/a_{1263} proposed by Carrillo-Colom in previous work [11]. It can be seen that these infrared ratios produce different values which represent spectral differences, due to the different structural conformation of regenerated cellulose fibres, which we will discuss later. Lyocell fibres have a higher crystallinity than viscose-type fibres. This is confirmed by the respective FTIR 1420/893 and 1278/1263 ratios, which show lower values for lyocell samples.

3.2. Comparative study of cellulose fibres upon mercerisation treatment

In the FTIR spectral region studied, significant differences in intensity and shape could be observed between the different samples after mercerisation. Viscose was the type most affected by this treatment, and reached dissolution at caustic soda concentrations higher than 16.7 g/100 ml. Moreover, after the treatment we could often observe a partial dissolution. The same observations could be made for the modal fibres, but the extent of the effects was less. For the lyocell sample, no physical differences or transformations were detected after the treatment.

The 1400–1200 cm⁻¹ spectral region of a series of mercerised cellulose fibres is shown in Fig. 2(a)–(c). This region includes the bands 1376, 1336, 1316, 1278, 1265, 1234 and 1227 cm⁻¹, assigned previously in Table 1. The intensity and shape evolution of these infrared absorbance bands define the structural changes caused by the caustic treatment.

The results of the infrared crystallinity ratios obtained for each fibre, as a function of different concentration of caustic treatment, are shown in Table 2.

From the tabulated values it can be noted that the TCI shows no significant changes for any of the samples. This infrared ratio, defined and contrasted by Nelson et al. by means of X-ray diffraction, indicated that the mercerisation process of the cellulose substrates without

Table 2
Infrared crystallinity indexes data on lyocell, modal and viscose, after caustic treatments

g/100 ml (NaOH)	1376/2902 (TCI)			1420/893 (LOI)*			1278/1263 (CCI)		
	Lyocell	Viscose	Modal	Lyocell	Viscose	Modal	Lyocell	Viscose	Modal
0	0.742	0.68	0.73	0.341 (80%)	0.54 (41%)	0.52 (49%)	0.66	1.17	1.02
6.2	0.715	0.68	0.72	0.387 (72%)	0.36 (77%)	0.35 (78%)	0.81	0.6	0.44
12.4	0.710	0.69	0.72	0.409 (68%)	0.37 (76%)	0.45 (69%)	0.86	0.65	0.90
14.5	0.748	0.64	0.74	0.421 (65%)	0.42 (65%)	0.49 (50%)	0.9	0.81	0.94
16.7	0.725	0.66	0.73	0.436 (62%)	0.45 (69%)	0.50 (48%)	1.09	1.08	1.07
18.0	0.761	–	–	0.472 (54%)	–	–	1.31	1.13	1.10
24.0	0.732	–	–	0.581 (30%)	–	–	1.18	1.19	1.37

* The values of the degree of crystallinity [14] are in parentheses.

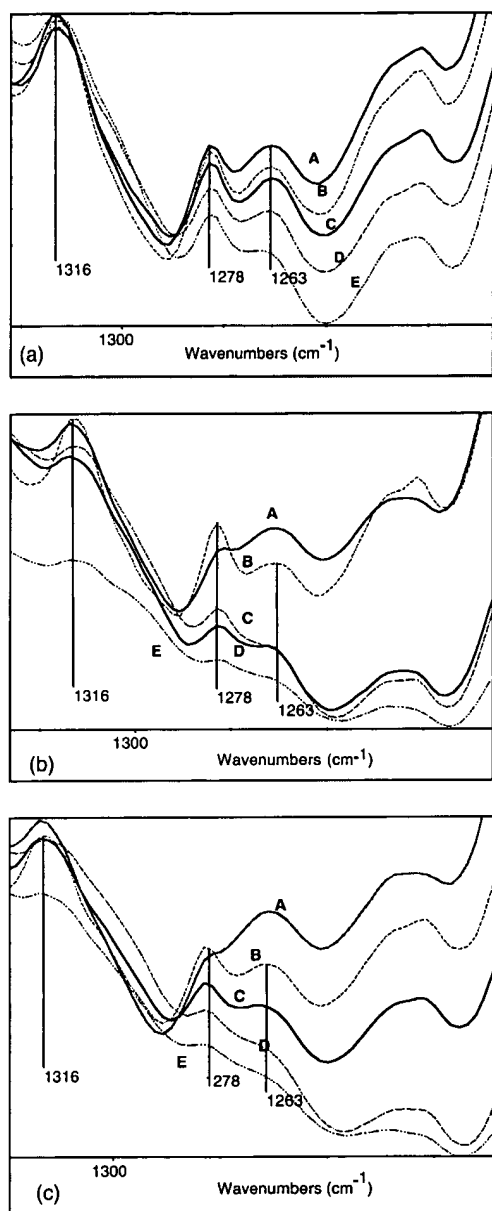


Fig. 2. Spectral area corresponding to: (a) lyocell, (b) modal, and (c) viscose fibres, illustrating the changes caused by the caustic treatments. (A: 0 g NaOH, B: 6.2 g NaOH, C: 12.4 g NaOH, D: 18.0 g NaOH, E: 24.0 g NaOH).

crystalline cellulose I content cannot be considered a reliable indicator of the structural changes occurring in the alkaline degradation process. Nevertheless, previous studies [12,13] of substrates with a high crystalline cellulose I content demonstrate that this ratio is useful to follow structural changes during caustic treatments.

However, the LOI and the 1278/1264 ratio bands allow us to follow structural changes caused by the mer-

cerisation stage. Both ratios were observed to have similar behaviour, although it should be pointed out that the 1278/1264 ratio was more sensitive in the case of the LOI.

Significant differences in behaviour can be discerned between the lyocell and the viscose type fibres. The lyocell fibre crystallinity decreases with increases in the concentration of the sodium hydroxide solution. Using the correlation proposed by O'Connor et al. to obtain the degree of crystallinity, by means of X-ray diffraction, according to Wakelin [14], it is evident from the LOI results that there is a decrease in the degree of crystallinity (in parentheses) of these fibres from 0.34 (80%) to 0.58 (30%).

Modal and viscose fibres show a completely different evolution of these infrared ratios. The initial degree of crystalline cellulose II is lower than that of lyocell: 41% for viscose and 49% for modal fibres. As is shown in Table 2, the LOI ratios reveal that there is initially a noticeable decrease, from 0.54 to 0.36 and 0.52 to 0.35 for viscose and modal respectively. This corresponds to an increase in crystallinity from 41% to 77% and 49% to 78% for the viscose and modal samples. Caustic concentrations of up to 12.4 g NaOH/100 ml produce a decrease in crystallinity until there is total dissolution at high concentrations of sodium hydroxide. The same behaviour is observed for the 1278/1264 relation bands. With this kind of viscose type fibre, the crystallinity of the untreated samples is initially below that of the pre-treated fibres, and there is evidence of a certain amount of recrystallization under alkaline conditions. The increase in crystallinity of viscose and modal fibres after treatment with sodium hydroxide has been observed by Sreenivasan et al. [15] and Rusznák et al. [16]. These authors explained the recrystallization as a mobilisation of the cellulose molecules by cleavage of hydrogen bonds. The later progressive decrease in the degree of crystallinity, at high caustic concentration, by the transformation of the crystalline structure from cellulose II to amorphous cellulose, disproves the possibility that this increase might be caused mainly by dissolution and removal of separate short chain fractions from the bulk fibrous system.

As this initial increase in crystallinity is not present in lyocell fibres, it could be said that modal and viscose fibres are made up of cellulose II, amorphous cellulose and a region of transitory structure caused by the collapse of the high-molecular chains that occurs during the spinning process. The alkali treatment produces a structural relaxation of these collapsed cellulose chains, which facilitates a new reorientation towards the crystalline structure of cellulose II.

The difference between solvent spun lyocell and the viscose type fibres is a result of the spinning process. In the old viscose processes, the dissolved macromolecules are completely disordered. During fibre formation not

only must they be oriented in order to form the crystallites, but decomposition must also take place in order to regenerate the cellulose derivative. With the dissolution of the new organic solvent cellulose, no decomposition is required and the dissolved macromolecules are already somewhat oriented before fibre formation. Orientation and structure formation is thus easier.

The viscose fibre spectrum obtained at high concentrations of sodium hydroxide (about 18 g/100 ml H₂O), shows that all the characteristic bands of the crystalline structure of cellulose II disappear, indicating the transformation to an amorphous structure. Concentrations up to 18 g NaOH/100 ml H₂O cause the dissolution of viscose forming a gel. For modal fibre the total transformation of cellulose II to amorphous cellulose takes place from 24 g NaOH/100 ml and it becomes a gel at sodium hydroxide concentrations higher than 30 g NaOH/100 ml. However, lyocell fibres retain part of the cellulose II formation at concentrations higher than 24 g NaOH/100 ml. This indicates that the structure of the lyocell fibre is more compact and prevents the distortion of the macromolecules by the penetration of swelling agents, thus providing its resistance to high caustic concentrations.

3.3. Analysis of the moisture regain

One can estimate the extent of less ordered regions in a fibre by evaluating moisture regain. Cellulose fibres with greater amorphous content absorb a greater quantity of water. Fig. 3 shows the moisture regain data evolution for the untreated samples and the samples mercerised by sodium hydroxide solutions. The percentage of moisture absorbed by the untreated fibres is less for the lyocell (12%) than for viscose type fibres (15%). This is as a result of the greater degree of crystallinity of the lyocell.

The changes in moisture regain for viscose type fibres and lyocell fibres is different. The lyocell fibres show increased and sustained moisture regain between 12% and 18%. The modal and viscose fibres, however, show similar behaviours, although they follow a significantly different development. At first the fibres have a constant value of moisture regain, even showing a decrease up to concentrations of 8 g NaOH/100 ml. At higher concentrations, the moisture regain increases up to a maximum value of 23% (18 g NaOH/100 ml) for viscose and 21.5% (21.5 g NaOH/100 ml) for modal. After these maximum values, a decrease follows due to the total dissolution of viscose and partial dissolution of modal samples.

These results support the observations from FTIR experiments. Lyocell fibres retain a smaller quantity of water because of their structure: high crystallinity and

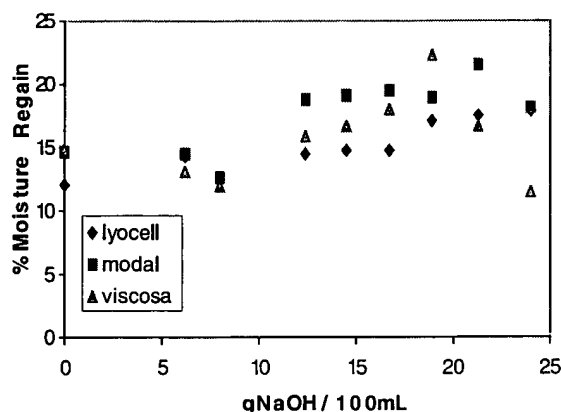


Fig. 3. Moisture regain changes for the different regenerated cellulose samples.

orientation are less affected by the swelling agent. However, the modal and mainly viscose fibres are more affected by the mercerisation process, reaching total dissolution at higher sodium hydroxide concentrations. The decreasing moisture regain value at low caustic concentrations for viscose type fibres indicates the initial recrystallization stage.

4. Conclusions

Like viscose type fibres, lyocell fibres consist of crystalline cellulose II and amorphous cellulose. Solvent spun lyocell fibres have a higher degree of crystallinity (80%) than the 49% and 41% crystallinity in the modal and viscose fibres respectively.

It has been observed that during the mercerisation treatment the viscose type fibres are more affected to the degradation caused by the transformation of crystalline cellulose II to amorphous cellulose, to the point of total dissolution at high caustic concentrations for modal and viscose. For lyocell fibres, this transformation is partial and dissolution at high concentration does not occur. This can be explained by the orientation and high crystallinity of the lyocell macromolecules. This property inhibits the effect of swelling agents and limits degradation.

The spinning process involved in viscose type fibres produces a transitory structure caused by the collapse of the high-molecular chains that has not been observed in lyocell. As a consequence, the treatment induces a relaxed structure in these collapsed cellulose chains at low alkali concentration, which facilitates reorientation towards the crystalline structure of cellulose II. This produces an increase in the crystallinity, as indicated by the

1420/893 (LOI) ratio along with the 1278/1263 ratio, as proposed by Carrillo and Colom.

The moisture regain results support the FTIR conclusions.

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